1. Study on Surface Electricity. (XVI)[1]

On the Theory of U-effect II (Continued)

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As was already mentioned before,[2] U-effect II is a phenomenon based on the capacity current of the interfacial double layer produced by the periodical change of the interfacial area with its mechanical vibration. This mechanism was proved by the fact that the output voltage of U-effect II in case of a single Hg-solution interface was a function of the applied d. c. polarizing potential, diminishing at the potential of the electrocapillary maximum,[3] where the surface electronic charge of mercury is zero or the integral capacity of the double layer is zero.

A perfect derivation of the equation describing this phenomenon has not been given as yet and we shall derive it in this article.

1. DERIVATION OF THE EQUATION

We shall treat the mercury-solution (without mercurous ion) interface as an ideal polarized electrode,[4] which behaves like a perfect condenser without leakage. In this sense the equivalent circuit of the interfacial phase in the element of U-effect II is given by a series combination of a condenser representing the double layer and a resistance representing the solution phase. The instantaneous capacitance c of this condenser can be written in

$$c = K + \Delta c, \qquad (1)$$

K being its average value and Δc its variable part, because the capacitance varies with the interfacial area, that is

$$\Delta c = (\varepsilon / 4\pi d)\Delta A,$$

where A is the interfacial area, ε the dielectric constant and d the distance between the two plates of the equivalent condenser, respectively. Of course there may be a phase retardation between the area change and the mechanical vibration of the element, but it is not important here as long as the conversion efficiency is not considered, and we shall take Δc or ΔA the independent variable in this treatise.

Now, considering the alternating component in this circuit only, we designate the potential drop at load in e and the current in i. All the symbols in small latine letters are the instantaneous values. R_0 in Fig. 1 is the equivalent series resistance

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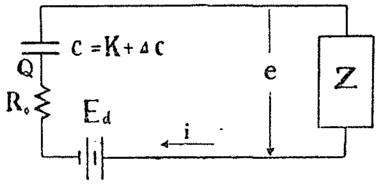

Fig. 1

(solution resistance) and E_a the d.c. potential difference of the two plates of the equivalent condenser, which is the sum of the applied potential and the volta-potential difference of the interface etc.

Now denoting the electrical charge of the condenser in Q, we get

$$i \equiv \frac{dQ}{dt} = \frac{d}{dt} \left[c(E_a+e-iR_0) \right]. \tag{2}$$

Substituting the definition of (1) into (2), we get

$$\begin{aligned} i &= \frac{d}{dt} \left[(K+\varDelta c)(E_a+e-iR_o) \right] \\ &= \frac{d}{dt} \left[KE_a \left(1+\frac{\varDelta c}{K}\right)\left(1+\frac{e-iR_o}{E_a}\right) \right] \end{aligned} \tag{3}$$

As the change of the interfacial area is very small compared with its average value,

$$\varDelta c/K = \varDelta A/A \ll 1,$$

and also

$$\frac{e-iR_o}{E_a} = \frac{Q\cdot \varDelta c - iR_o}{Q\cdot K} \leqq \frac{\varDelta c}{K} \ll 1,$$

iR_o being positive. Hence, we can neglect the small terms of more than second order in developing (3), and we get

$$i = \frac{d}{dt} \left[K(E_a+e-iR_o) \right] + \frac{d}{dt} \left[E_a(K+\varDelta c) \right].$$

Now, as we are not concerning the transient phenomena, the complex representations in a.c. theory are introduced, *i.e.*

$$\begin{aligned} i &= \sqrt{2}\underset{\bullet}{I}e^{j\omega t} \\ e &= \sqrt{2}\underset{\bullet}{E}e^{j\omega t} \\ \varDelta c &= \sqrt{2}\underset{\bullet}{\varDelta C}e^{j\omega t}, \end{aligned}$$

where the phase factors are included in the (complex) amplitude terms. These are substituted in the above equation and differentiation is performed, giving

$$\underset{\bullet}{I} = j\omega K\underset{\bullet}{E} - j\omega KR_o\underset{\bullet}{I} + j\omega K\cdot \frac{E_a}{K} \cdot \underset{\bullet}{\varDelta C},$$

or

$$\dot{I}=j\omega K\dot{E}-j\omega KR_o\dot{I}+j\omega K\dot{V}, \tag{4}$$

where

$$\dot{V}\equiv E_a\cdot\frac{\Delta \dot{C}}{K}\left(=\frac{qdA}{dt}\right)$$

is an alternating voltage which is to appear at the load terminals when the load is absent, that is, the electromotive force in U-effect II. q is the interfacial charge density, or

$$q=dQ/dA.$$

In the differential calculus we assumed the constancy of E_a. This includes the absence of time-lag in the formation of the interfacial double layer, which is considered to hold within the frequency region in our case.[4]

Equation (4) can be rewritten in

$$\dot{E}=R_o\dot{I}+\frac{\dot{I}}{j\omega K}-\dot{V}. \tag{5}$$

While, Ohm's law states

$$\dot{E}=-\dot{I}Z, \tag{6}$$

where Z is the load impedance. Equating (5) and (6), we get

$$\dot{I}=\frac{\dot{V}}{R_o+Z+\dfrac{1}{j\omega K}},$$

or, when we describe Z in resistance and reactance terms, *i. e.* $Z=R+jX$, we get

$$\dot{I}=\frac{\dot{V}}{(R_o+R)+j\left(X-\dfrac{1}{\omega K}\right)}, \tag{7}$$

which is nothing but the phenomenological formula of U-effect II.

The appearance of the equation (7) readily shows that this circuit is equivalent

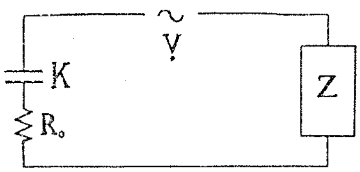

Fig. 2

to a series circuit of the interfacial impedance (K and R_o) and the load with electromotive force $\dot{V}$ (Fig. 2). Equation (7) is easily given from Ohm's law applied to this circuit. An assumption was made in the above derivation that $\Delta A \ll A$ held, which is correct in almost every cases in our experiments.

On the other hand, this circuit can be considered to be a sort of frequency modulation circuit,[5] as it includes capacity change. This is a special case of it, where the carrier frequency equals the signal frequency, though the modulating frequency $\Delta\omega$ satisfies the ordinary condition, *i.e.*

$$\Delta\omega/\omega \ll 1.$$

The general analysis of L-C circuit including capacity change was performed by Barrow, [6] who got a Hill-type differential equation[7] solved only in approximation. Although this method of analysis can also be applied in our case, we shall not refer to it, as our present purpose does not demand it.

2. APPLICATION

Equation (7) gives various suggestions on the application of U-effect II, and we shall describe on them in two cases, one is already known and the other will be described in detail in the next article.

(1) **Impedance matching.** When the load resistance is resistive, i.e. $X=0$ and $Z=R$, the power supplied to the load is given by

$$P = I^2R = \frac{V^2R}{(R_o+R)^2+\frac{1}{\omega^2K^2}} \quad ,$$

where I and V are the moduli of $\dot{I}$ and $\dot{V}$, respectively. The condition of maximum power with variable R is given by

$$\partial P/\partial R = 0,$$

or

$$R_0^2 + \frac{1}{\omega^2K^2} = R^2.$$

This equation says that it is when the inner impedance and the load resistance have equal moduli that maximum power is supplied to the latter.

This principle was already discovered in the name of the "Impedance matching method" by the present authors,[8] and was used in measuring the interfacial capacities of the electrical double layers and also the inner impedance of the element of U-effect II. The details of the experimental devices of this method were given in the same authors' papers concerning them.[8]

(2) **Resonance.** When we put $X=\omega L$ in equation (7), L being the inductance of

load, we get

$$\dot{I} = \frac{\dot{V}}{(R_o+R)+j(\omega L-\frac{1}{\omega K})} \; .$$

This gives maximum value of I, when

$$\omega L = 1/\omega K,$$

which is nothing but the series resonance condition, and this principle is equally applicable for the determinations of the interfacial double layer capacities, the details of which will be described in the next article.

SUMMARY

U-effect II is a phenomenon of the periodical charging and discharging of a varying interfacial capacitance, for which the equation representing the current produced by it was derived. This equation shows that this circuit is approximately equivalent to a series combination of a condenser, a resistance and a load. With resistive load we can give the condition of maximum power transfer (impedance matching), and with inductive load we get a series resonance condition, both of which can be used for the determination of the interfacial double layer capacities.

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REFERENCES

(1) Read before the semi-annual meeting of the Institute, held on Nov. 28, 1952.
(2) S. Ueda, A. Watanabe and F. Tsuji, This Bulletin, 18, 108 (1949); 19, 44 (1949) ; **20,** 28 (1950).
(3) A. Watanabe and S. Ueda, *J. Electrochem. Soc. Japan*, **20,** 248, 308, 358, 419 (1952).
(4) See reference (3).
(5) S. Ueda, A. Watanabe and F. Tsuji, This Bulletin, **28,** 47 (1952) ; K. Maeda and T. Hayashi, "Frequency Modulation", (in Japanese), Shukyo-sha, (1946).
(6) W. L. Barrow, *I. R. E.*, **21,** 1182 (1933).
(7) G. N. Watson and E. T. Whittaker, "Modern Analysis", p. 404 (1935).
(8) S. Ueda, A. Watanabe and F. Tsuji, This Bulletin, **24,** 12 (1951) ; **25,** 30 (1951) ; **29,** 32 (1952).
(9) *e.g.* T. Hotari, "Electrical Circuit" (in Japanese), p. 77, Shukyo-sha (1936).